

## A SIMPLE CONVERSION OF N,N-DIMETHYL-2-ALKENYLAMINE TO 2-ALKENAL

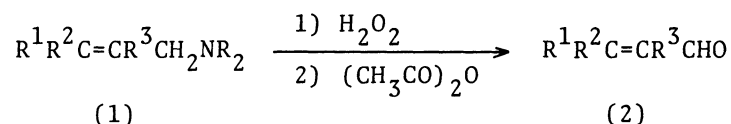
Kunihiko TAKABE,\* Takashi YAMADA, and Takao KATAGIRI

Department of Synthetic Chemistry, Faculty of Engineering,  
Shizuoka University, Hamamatsu 432

Treatment of N,N-dimethyl-2-alkenylamine with 30% H<sub>2</sub>O<sub>2</sub> followed by acetic anhydride affords 2-alkenal ( $\alpha,\beta$ -unsaturated aldehyde) in good isolated yield.

N,N-Dialkyl-2-alkenylamines (1), which are easily prepared by the alkali-metal catalyzed telomerization of 1,3-diene with dialkylamine<sup>1)</sup>, are useful intermediates in organic synthesis. Recently a variety of methods are available for the transformation of (1) into 2-alkenol,<sup>2)</sup> 2-chloroalkene,<sup>3)</sup> 2-alkenyl phenyl selenide<sup>4)</sup> and optically active enamine.<sup>5)</sup>

A simple, selective procedure for the conversion of (1) to 2-alkenal ( $\alpha,\beta$ -unsaturated aldehyde) (2) via the Polonovsky reaction<sup>6)</sup> is presented here.

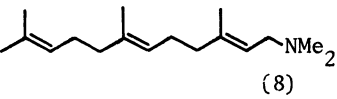
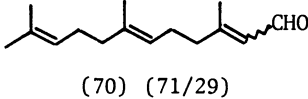
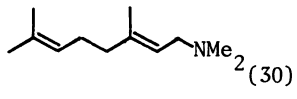
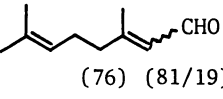
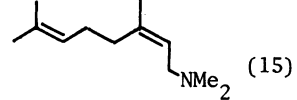
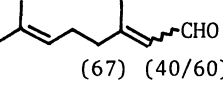
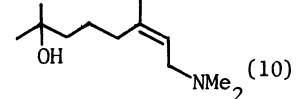
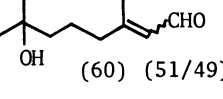
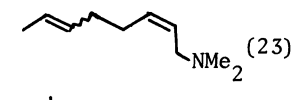
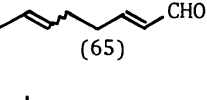
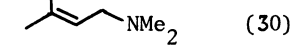
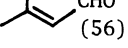


N,N-Dimethyl-2-alkenylamine (1) reacts with excess 30% H<sub>2</sub>O<sub>2</sub> in methanol. Degradation of excess of H<sub>2</sub>O<sub>2</sub> with PtO<sub>2</sub>, and evaporation of the reaction mixture under reduced pressure (to remove H<sub>2</sub>O and methanol) provides the corresponding amine oxide in quantitative yield. Conversion of the amine oxide to 2-alkenal (2) is conveniently achieved by adding acetic anhydride. Accordingly, the crude amine oxide is diluted with the solvent, and reacts with 1 - 3 mol. equiv. of acetic anhydride at room temperature. The reaction is clean and complete in less than 1 hr, providing 2-alkenal (2) in good isolated yield (56 - 76% yield based on the starting amine). The ratio of 2-(E)/2-(Z) of 2-alkenal obtained by this method depend extremely on the structure of the starting amines (1).

The results are summarized in Table.<sup>7)</sup>

Table Conversion of N,N-dimethyl-2-alkenylamine (1) to 2-alkenal (2)

$$R^1R^2C=CR^3CH_2NR_2 \xrightarrow{\text{Step 1}} [R^1R^2C=CR^3\overset{O}{\underset{||}{C}}CH_2NR_2] \xrightarrow{\text{Step 2}} R^1R^2C=CR^3CHO$$

Step 1 <sup>a)</sup>			Step 2 <sup>b)</sup>		
(1) (mmol)	30% H <sub>2</sub> O <sub>2</sub> (ml)	CH <sub>3</sub> OH (ml)	(CH <sub>3</sub> CO) <sub>2</sub> O (mmol)	Solvent (ml)	(2) Yield(%) <sup>c)</sup> (2E/2Z)
 (8)	8	15	25	Benzene 10	 (70) (71/29)
 (30)	5	15	90	Et <sub>2</sub> O 20	 (76) (81/19)
 (15)	5	15	45	Benzene 10	 (67) (40/60)
 (10)	5	10	50	Benzene 5	 (60) (51/49)
 (23)	17	40	70	Benzene 10	 (65)
 (30)	17	80	90	Et <sub>2</sub> O 20	 (56)

a) 24 h at room temp. b) 1 h at room temp. c) isolated yield

#### References

- 1) K. Takabe, T. Katagiri, and J. Tanaka, *Tetrahedron Lett.*, **1972**, 4009, *idem.*, *Bull. Chem. Soc. Jpn.*, **46**, 222 (1973).
- 2) V. Rautenstrauch, *Helv. Chim. Acta*, **56**, 2492 (1973), K. Takabe, T. Katagiri, and J. Tanaka, *Tetrahedron Lett.*, **1975**, 3005.
- 3) K. Takabe, T. Katagiri, and J. Tanaka, *Chem. Lett.*, **1977**, 1025.
- 4) S. Murahashi and T. Yana, *J. Am. Chem. Soc.*, **102**, 2456 (1981).
- 5) K. Tani, T. Yamagata, S. Otsuka, S. Akutagawa, H. Kumobayashi, T. Taketomi, H. Takaya, A. Miyashita, and R. Noyori, *J. Chem. Soc., Chem. Commun.*, **1982**, 600.
- 6) For a recent review; M. Ikeda and Y. Tamura, *Yuki Gosei Kagaku Kyokai Shi*, **38**, 10 (1980) and references cited therein.
- 7) The structures of all compounds were verified by compatible spectral data.

(Received September 24, 1982)